

The University of Chicago

ISOTOPE EFFECT AND QUENCHING
IN THE
FLUORESCENCE OF BROMINE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYS-
ICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1937

By

HAROLD JAMISON PLUMLEY

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from THE PHYSICAL REVIEW, Vol. 45, No. 10, May 15, 1934

The University of Chicago

ISOTOPE EFFECT AND QUENCHING
IN THE
FLUORESCENCE OF BROMINE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYS-
ICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1937

By
HAROLD JAMISON PLUMLEY

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from THE PHYSICAL REVIEW, Vol. 45, No. 10, May 15, 1934



Isotope Effect and Quenching in the Fluorescence of Bromine

HAROLD J. PLUMLEY, *Ryerson Laboratory, University of Chicago*

(Received March 23, 1934)

The fine structure of the resonance spectrum of bromine excited by the green line of the mercury arc has been photographed and a theoretical explanation obtained in terms of the three molecular isotopes present and the values of the rotational and vibrational quantum numbers for the transitions. In addition, the fluorescence intensities in bromine were studied as a function of the pressure, for three spectral regions. The much lower intensities in

bromine as compared with iodine are accounted for on the basis of less initial absorption, and of greater quenching, due to the longer mean lifetime of the molecule in the upper state. The fluorescence data are concordant with results obtained in the analysis of bromine's absorption spectrum. The green mercury line did not excite any observable fluorescence in gaseous chlorine. This result is shown to be in accordance with the theoretical predictions.

INTRODUCTION

ALTHOUGH resonance spectra have been observed for many diatomic molecules, it would seem that only in the cases of iodine and oxygen¹ have any complete analyses been carried out. The bromine resonance spectrum, previously photographed by the writer under low dispersion,² has now been obtained under a dispersion sufficient to resolve the line structure of the different "orders" of fluorescence. A careful analysis appeared desirable since it would not only be interesting because of the presence of isotopes in bromine, but also because it would allow a detailed comparison to be made of the behavior in fluorescence of the two closely related molecules, bromine and iodine. There have been numerous papers published on the interpretation of the iodine resonance spectrum, but the most recent and complete is one by F. W. Loomis,³ whose methods will in part be followed here.

EXPERIMENTAL PROCEDURE

The apparatus customarily used in the production of resonance spectra was found to be entirely inadequate in the excitation of the bromine fluorescence, which is about 300 times weaker than that of iodine. The modifications made for the purpose of this experiment may be seen in

Fig. 1. The mercury arcs were constructed to illuminate the entire length of the tube (70 cm). This was accomplished by bending the anode ends, where the arcs are of low intensity, out from the resonance tube. While running, the arcs were constantly under evacuation with a diffusion pump. By maintaining a strong current of air over the anode ends, it was possible to pass eight or more amperes through each arc.

For the purposes of the analysis it proved necessary to greatly weaken the two yellow lines of the mercury spectrum. This was accomplished by the use of two long thin absorption cells, 1×4 cm in cross section, containing saturated neodymium chloride solution. The flat Pyrex tubing from which these cells were made is now available from the Corning Glass Works. The central tube of the light furnace, containing the bromine vapor, was 4 cm in diameter. One end was drawn into a horn and blackened, a design due to R. W. Wood, while the other end was constricted to form a stop, then flared out to provide a ground glass table. Upon this was placed a glass plate to which the prism was attached by balsam. The lower surface of the glass plate was the only one to scatter the mercury radiation, and the plate was easily removable for cleaning. The entire apparatus was enclosed in a sheath of aluminum foil which necessitated circulating water in 4 mm tubing through the neodymium chloride solution to prevent boiling.

Depending on the density required, plates were obtainable in from 10 to 70 hours on a

¹ F. Rasetti, *Proc. Nat. Acad. Sci.* **15**, 411 (1929).

² H. Plumley, *Phys. Rev.* **43**, 495 (1933).

³ F. W. Loomis, *Phys. Rev.* **29**, 112 (1927).

Steinheil three prism spectrograph. Only Ilford Hypersensitive Panchromatic plates were found to be of sufficient sensitivity to record the spectrum satisfactorily. It is interesting to note that the presence of the water-cooled filters materially increased the intensity of the fluorescence in spite of causing an undoubted decrease in the intensity of the exciting radiation. This may be ascribed to the fact that without the filters the bromine acquires a high temperature, and the higher vibrational levels which contribute most to reabsorption of the emitted light become more populated.

ANALYSIS OF THE FLUORESCENCE SERIES

It is convenient to adopt the nomenclature of Loomis and Wood in designating the fluorescence series. A long series of doublets is observed on the long wave-length side of the exciting line.

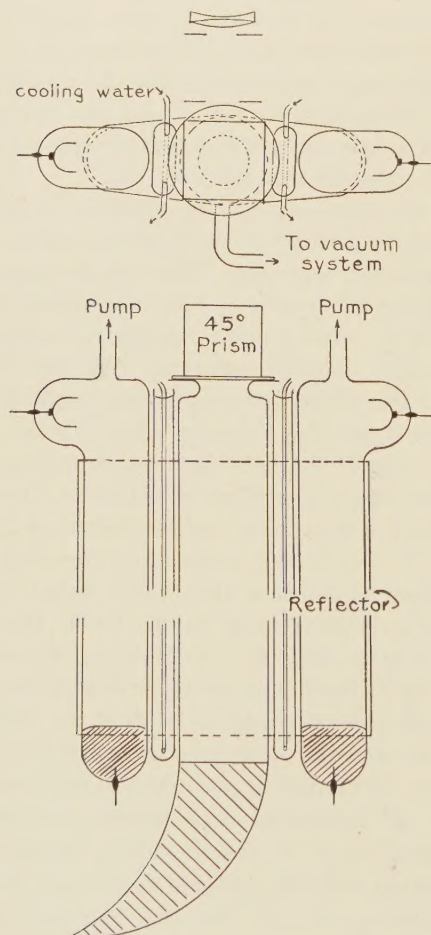


FIG. 1. Diagram of the light furnace.

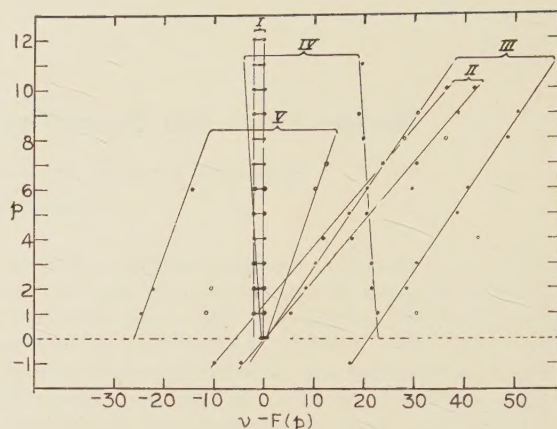


FIG. 2. Fluorescence series with intensities indicated by blackness of points.

These are numbered consecutively, starting with zero at the position of the exciting line, to give p , the "order" of the doublet. In the event that "antistokes" doublets appear on the short wave-length side, these are similarly designated except that p takes negative values.

In the case of iodine the broadened green line of the high temperature quartz arc is required, if more than one series of doublets is to be excited. In bromine, however, due to the isotope situation, which multiplies the number of absorption lines, the relatively narrow green line of the ordinary mercury arc is of sufficient width to excite five series of doublets. The most intense of these, which we will call the main series, is only possibly resolved in the lowest orders (values of p) and not at all in the higher orders, due to the decrease in dispersion at longer wave-lengths. The overlapping by a member of another doublet series makes the resolution extremely difficult in any case (see Fig. 2).

By the use of type "N" infrared sensitive plates this series has been followed out to the 17th order; no antistokes members are present. In Table I are given the frequencies, in cm^{-1} , of the main series lines, 1.5 wave numbers being added to all values to give what would be the high frequency component of the doublet, if it were resolved in every case. The values are represented within experimental error up to the 10th order by the formula:

$$\nu_p = 18,469.22 - 323.81(v'' + \frac{1}{2}) + 1.15(v'' + \frac{1}{2})^2.$$

TABLE I. Frequencies (cm^{-1}) of main series lines.

Order	Wave-length	Observed frequency	Calculated frequency	Difference
0	5460.7	18307.5	18307.5	0.0
1	5558.4	17985.7	17986.2	-0.5
2	5659.2	17665.4	17666.9	-1.5
3	5762.5	17348.8	17349.9	-1.1
4	5868.2	17036.3	17035.3	1.0
5	5978.1	16723.2	16723.0	0.2
6	6091.1	16413.0	16413.0	0.0
7	6207.5	16105.3	16105.3	0.0
8	6327.6	15799.7	15799.9	-0.2
9	6451.2	15497.0	15496.8	0.2
10	6579.3	15195.0	15195.9	-0.9
11	6712.7	14893.2	14897.5	-4.3
12	6849.8	14594.9	14601.2	-6.3
13				
14	7133.0	14015.0 ± 10		
15	7287.1	13719.3 ± 10		
16				
17	7597.0	13160 ± 10		

This is in good agreement with the vibrational constants given in Jevons' *Report on Band Spectra*, namely, $\omega_e'' = 323.86$ and $x_e''\omega_e'' = 1.15$. It is evident from the fluorescence data that these constants hold only for low values of v'' and that higher terms are required to give the higher levels accurately (see "Difference" in Table II).

In Fig. 2 the fluorescence spectrum is plotted following the scheme of Mecke.⁴ The ordinate is p , the order of a group, and the abscissa is $\nu - F(p)$ where ν is the frequency of any line and

$$F(p) = 18,307.5 - 322.67p + 1.15p^2.$$

This is, of course, equivalent to the vibrational formula just given. The five doublet series are then given empirically by:

$$\begin{aligned}\nu_{\text{I}} &= F(p) + (-3.0), \\ \nu_{\text{II}} &= F(p) + 4.3p + (-6.0), \\ \nu_{\text{III}} &= F(p) + 3.35p + (+20.5), \\ \nu_{\text{IV}} &= F(p) - 0.4p + (+24.0), \\ \nu_{\text{V}} &= F(p) + 1.65p + (-25.0).\end{aligned}$$

The quantities in the parentheses are the doublet intervals, d . They are to be omitted to give the expressions for the main lines and are to be included to give the expressions for the companion lines in the case of each doublet. The coefficient of p is γ , the slope of the line in Fig. 2.

In the initial absorption process, which precedes the resonance emission, the values of J'' for a P transition and for an R transition, respectively, are found by the following two equations.

$$d_P = B_v''(4J'' - 2); \quad d_R = B_v''(4J'' + 6).$$

The certainty in the calculation of the J 's is limited by the experimental error in the determination of the d 's. If a series arises from a P transition in absorption, the companion line of the doublet, when extrapolated to the zero order in Fig. 2, will lie on the high frequency side of the exciting line; if from an R transition, the companion line will lie on the low frequency side.

From the work of W. G. Brown⁵ on the absorption spectrum, we may assign the v' , v'' transition for each doublet series. This assignment is not ambiguous because we know the value of v'' from the number of observed anti-stokes lines. As a check on our assignments we may calculate the positions of the band origins by the following equation, where 18,307.5 is the frequency of the exciting line, in this case the mercury green line.

$$\nu_{\text{origin}} = 18,307.5 - B_v'J'(J' + 1) + B_v''J''(J'' + 1).$$

TABLE II. Calculated and observed values of γ .

Series designation	Initial transition	Isotope	Position of band head from fluorescence	Position of band head from absorption	Calculated γ	Observed γ
I	19,0 R(8)	79,81	18309.2	18310.9	0.0	0.0
II	23,1 R(17)	81,81	18316.7	18319.6	+4.28	+4.3
III	25,1 P(64)	79,81	18466.6	18477.5	+3.41	+3.35
IV	21,0 P(74)	79,79	18509.9	18501.2	-0.42	-0.4
V	21,0 R(76)	79,81	18503.3	18490.4	+1.58	+1.65

These are compared with the ν_{head} values found by Brown in Table II. The rotational constants of bromine are such that the band heads and band origins are practically coincidental. The origins calculated from fluorescence data are only accurate to about 5 cm^{-1} , while the heads observed in absorption may be in error by as much as 10 cm^{-1} , since it is scarcely possible to identify the isotope shift in this region.

⁴ Mecke, *Zeits. f. Physik* 7, 73 (1921).

⁵ W. G. Brown, *Phys. Rev.* 38, 1179 (1931).

Kratzer and Sudholt⁶ have developed the following formula for γ , where the subscript 0 refers to the main series and the subscript i to any other fluorescence series. This equation holds only in the absence of isotopes.

$$\gamma_i = 2x_e''\omega_e''(v_i'' - v_0'') + \alpha''(J_i''^2 - J_0''^2).$$

In this equation α'' is the usual rotational constant in:

$$B_v'' = B_0'' - \alpha''v''.$$

In bromine, however, it is the isotope effect which is the chief factor in the determination of γ . The complete expression, including the isotope effect, then becomes the following, where ρ is the square root of the ratio of the reduced masses; $\rho = 1.00623$, 1.00000 , and 0.99373 for $\text{Br}_2^{79,79}$, $\text{Br}_2^{79,81}$, and $\text{Br}_2^{81,81}$, respectively. It will be noted that the reference series, I , belongs to $\text{Br}_2^{79,81}$.

$$\begin{aligned} \gamma_i = & x_e''\omega_e''[(2v_i'' + 1)\rho^2 - (2v_0'' + 1)] \\ & + \alpha''(\rho^3 J_i''^2 - J_0''^2) - \omega_e''(\rho - 1) \\ & + p x_e''\omega_e''(\rho^2 - 1). \end{aligned}$$

The last term would have the effect of giving a slight curvature, in Fig. 2, to the line corresponding to an isotope molecule. To allow for this and to obtain a theoretical value for the observable γ in Fig. 2, p may be set equal to five in this expression, giving the mean slope for the range of data used. Values of γ calculated in this way are compared in Table II with those experimentally observed. For each fluorescence series there proves to be only one possible isotope assignment which theoretically will give the observed value of γ .

Series of doublets are also excited by the yellow lines of the mercury arc. To observe these it is merely necessary to replace the neodymium chloride solution in the filter cells by a solution of potassium dichromate. Most of these series have two antistokes members, which is in accordance with the v'' numbering of the stronger absorption bands in the yellow region. An analysis of these series was not attempted. The analysis would in any case be difficult since it is not always possible to say definitely from which of the mercury yellow lines a resonance line arises.

INTENSITIES IN THE FLUORESCENCE OF BROMINE

When the resonance spectrum of iodine was first observed, it was noticed that the maximum of fluorescence occurred at a pressure of 0.2 mm, while at higher pressures the fluorescence became

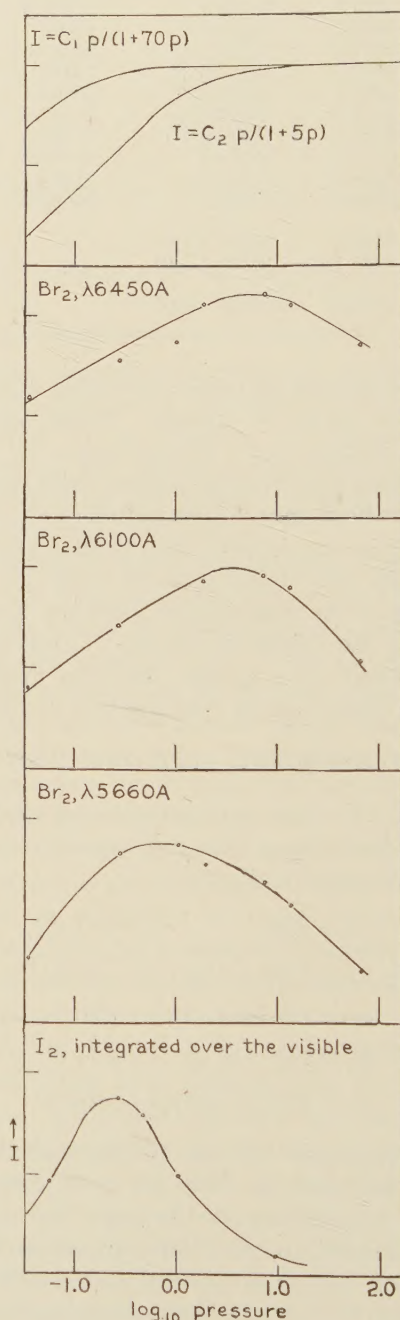


FIG. 3. Fluorescence intensities plotted against the logarithm of the pressure in millimeters.

⁶ Kratzer and Sudholt, Zeits. f. Physik 33, 147 (1925).

extremely weak. This effect was ascribed partly to reabsorption of fluorescence light by the vapor but mainly to quenching, and this became one of the criteria of a resonance spectrum, namely that it occur at very low pressures. In the event that the spectra were obtained at higher pressures, they were sometimes spoken of as transition cases from resonance spectra to Raman spectra. The fluorescence of oxygen at one atmosphere and of sulfur⁷ at 250 mm have been put into this category, although this seems doubtful.

The error in this argument becomes clear in the case of bromine. Several writers have given it as their opinion that bromine's fluorescence should be much less than that of iodine since it could only be observed at pressures around 0.001 mm. As a matter of fact, the fluorescence of bromine in the red portion of the spectrum is here found to be almost as intense at 75 mm as at any lower pressure. The explanation lies in the fact that the observed intensity depends not only on the concentration of the molecules present and on the quenching, but also decidedly on the amount of reabsorption of the fluorescence. This is shown in Fig. 3, where intensity, I , is plotted against the logarithm of the pressure in mm, p .

EXPERIMENTAL

The curves of Fig. 3 were obtained by taking a series of one hour photographs of the bromine resonance spectrum under identical conditions, varying only the pressure of the bromine. A Zeiss constant deviation spectrograph was used. All of the exposures were made on pieces taken from one large Ilford Panchromatic plate. The various pressures were obtained by utilizing the temperature-vapor pressure characteristics of bromine. It is known that the pressure of bromine in a closed system is at all points equal to its vapor pressure at the temperature of the coldest portion of the system. It was merely necessary to maintain, in communication with the light furnace, a reservoir at the temperature corresponding to the pressure of bromine desired. Various constant temperature baths were used for this purpose.

Microphotometer traces were made of all of the plates and the photographic densities deter-

mined by measurement of the traces. The densities were reduced to intensities by using the characteristic curve for the plate. Since the characteristic curve was not known exactly, the intensity values are not to be regarded as being strictly quantitative.

THE INTENSITY FUNCTION

In a purely theoretical case with no reabsorption, the intensity of fluorescence would be a function only of the absorption coefficient, the concentration, and the quenching factor. If a and c are constants, k_e the absorption coefficient for the wave-length of the exciting line, and τ the mean life of the molecule in the upper state in the absence of collisions, we would have the following equation, for the case, which holds approximately in our experiment, that only a small fraction of the incident radiation is absorbed.

$$I = ck_e p / (1 + a\tau p).$$

With the assumption that every collision is inelastic, the constant, a , is proportional to the square of the "collision radius" of the molecule. The factor of quenching, $1/(1 + a\tau p)$ is due to Stern and Volmer.⁸

This means that with no reabsorption, the intensity increases with increasing p , and approaches $ck_e/a\tau$ asymptotically, in spite of the increase in quenching with pressure. To correct for reabsorption, a factor which is less than one and diminishes with increasing p must be added. The resulting expression is:

$$I = [ck_e p / (1 + a\tau p)] f(p, k_{\lambda,s}).$$

In this equation k_{λ} is the absorption coefficient for the wave-length of fluorescence, which varies with the spectral region under observation, while k_e is the absorption coefficient for the wave-length of the exciting line, which is, of course, constant for any set of resonance series.

It should be noted that there is only one other possible factor which might be added to this expression; namely one involving a spontaneous predissociation of the bromine molecule in the upper state. In the absence of an external magnetic field this phenomenon is highly improbable in bromine and iodine.

⁷ B. Rosen, *Zeits. f. Physik* **43**, 116 (1927).

⁸ Stern and Volmer, *Phys. Zeits.* **20**, 183 (1919).

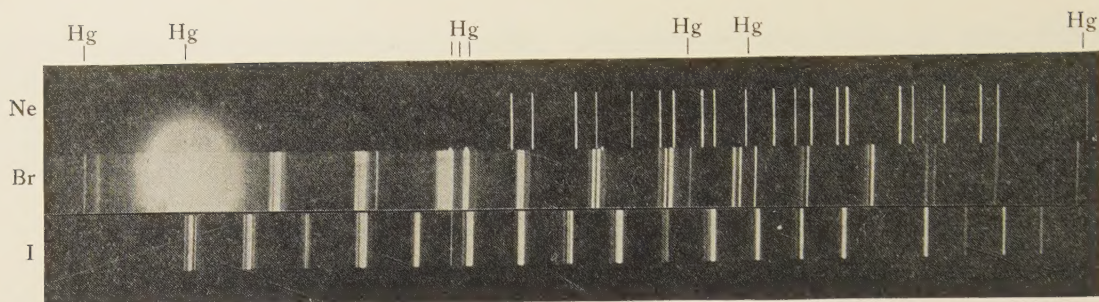


FIG. 4. Fluorescence of bromine and iodine compared showing the relatively greater development of the "collision" spectrum in bromine. The resolution is diminished by the use of a wide slit. The excitation is principally by the mercury green line, but partly by the yellow lines. The exposure was 60 hours in the case of the bromine and 10 minutes in the case of the iodine.

In Fig. 3 it is shown how the I vs. $\log p$ curves change in going from a case where the reabsorption term is one of great importance, namely the case of iodine, through the case of bromine, whose absorption coefficient is much less than that of iodine, to the theoretical case of no reabsorption. In bromine the absorption is greatest in the green and far less in the red. By determining the intensities photographically, it was possible to get separate curves for the different regions of the resonance spectrum (the second, fifth, and ninth "orders") and in this way to demonstrate the effect of decreasing reabsorption. The iodine intensity curve was constructed from photometric data by R. W. Wood.⁹ All of the curves in Fig. 3 were adjusted to nearly the same peak height by a suitable factor. It is at once apparent that it is reabsorption and not quenching which causes the decreased intensity at high pressures.

The theoretical case of no reabsorption is seen to be actually approached experimentally. That the bromine intensity curve in the red does not completely resemble the theoretical curve may be ascribed to the fact that the condition restricting the fractional absorption of incident light, which was put on the intensity equation, is no longer fulfilled at high pressures.

Under identical conditions, roughly 300 times as long an exposure is required to obtain a photograph of the bromine resonance spectrum as is required to get one of equal density of the iodine spectrum. This may now be explained.

If we take the average absorption coefficient of bromine, integrated over the spectral region which incloses the electronic band system involved in the fluorescence, and compare it to the

absorption coefficient of iodine obtained in the same way, we find them to be in the approximate ratio of 1 : 6. Now this mean absorption coefficient, which may be called k_m , is a measure of the transition probability to the upper states, and should usually be approximately proportional to the total transition probability from there to the lower states. But the transition probability from the upper states to the lower states is inversely proportional to the mean natural life of a molecule in the upper state. Since, in the limit with increasing pressure, $I = ck_e/a\tau$, it follows that the intensity of a resonance spectrum for high pressures is roughly proportional to $k_e k_m/a$ or to $k_e k_m/r^2$, where r is the collision radius.

For resonance spectra excited by the mercury green line, the value of k_e for iodine is twenty times as great as for bromine. Similarly, the value of k_m for iodine, as mentioned above, is six times as great as the value for bromine. Now if the collision radius for bromine is assumed to be the same as that for iodine, and if the effect of the difference in the amount of reabsorption in the two cases be neglected, we arrive at 1 : 120 as the ratio of the intensities of the resonance spectra. This value is at least of the order of magnitude of the experimentally determined ratio, which is about 1 : 300. The theoretical ratio may be made to check the experimental value exactly by assuming that the collision radius in bromine is 1.6 times the collision radius for iodine. However, this method of determining the ratio of the collision radii is scarcely justified due to the high possible error in the other factors which contribute to the ratio of the fluorescence intensities. In using k_m as a measure of the transition probability to the upper states, there may be considerable error introduced, since the relative

⁹ R. W. Wood, *Researches in Physical Optics*, Part II, p. 79.

positions of the upper and lower $U(\nu)$ curves in bromine and in iodine are not exactly similar, the upper state curve in bromine lying less directly over the lower state curve than is the case in iodine.

There is some reason to believe that for the determination of the transition probability to the lower states all of the absorption coefficients should be weighted by a factor of ν^2 , before integration to obtain the mean coefficient, k_m . This arises from the necessity of dividing an absorption coefficient by ν to obtain Einstein's B , the probability of a forced transition, and then multiplying by ν^3 to obtain Einstein's A , the probability of a spontaneous transition, which is the probability that determines the lifetime in the excited state. The ratio between the k_m 's for iodine and bromine obtained in this way is only slightly lower than the value given above.

The theoretical cases of no reabsorption are shown in Fig. 3 for two substances whose values for $a\tau$ are in the ratio 1 : 14. It is evident that the greater the absorption coefficient, the greater will be the slope of the intensity-pressure curve on the low pressure side of the peak. It is also true that with a high absorption coefficient the slope on the other side of the peak will be greater, because the reabsorption factor will become more important. The experimental data plotted in Fig. 3 give a qualitative substantiation of these conclusions.

Some evidence that the value of τ for the upper state in bromine is actually greater than in iodine is shown in Fig. 4, where the fluorescence spectra of the two elements, taken under identical conditions except for exposure times, are shown in coincidence. Although the spectra are roughly of equal density, the presence of faint bands in the background of the bromine plate is noticed, whereas these are absent in iodine. These bands constitute the so-called "collision" spectrum, in this case developed in the absence of any foreign gas. They are also obtained in iodine if a considerably longer exposure be given. It would seem that relative to the number of fluorescent transitions, there are more preceded by collisions in the upper state in bromine than in iodine.

AN ATTEMPT TO EXCITE A RESONANCE SPECTRUM IN CHLORINE

Since chlorine has a line absorption spectrum

in the region of the mercury green line, it might be thought that the mercury arc should excite a resonance spectrum in the gas. However, the absorption coefficient of chlorine for the mercury green line is of the order of 1000 times less than the coefficient in the case of bromine for this wave-length. The absorption coefficients are not obtained from absorption *vs.* wave-length curves but are the coefficients obtained experimentally by using the mercury arc as a source. This eliminates the error which would otherwise arise from the line nature of the absorption.

The fluorescence intensity expressions developed for bromine and iodine should hold for all of the halogens. From these it follows that the resonance fluorescence of chlorine should be extremely weak. To test this conclusion an attempt was made to excite fluorescence in chlorine by using the apparatus described in this paper. Under conditions capable of detecting fluorescence 300 times weaker than that of bromine (or about 100,000 times weaker than that of iodine) no trace of a resonance spectrum was obtained. Pressures from 0.2 mm to one atmosphere were tried. The lowest pressures were determined by means of a Pirani gauge, which is well adapted to work with the halogens. The higher pressures were measured with an oil-mercury manometer.

It is interesting to note that Bhagavantam,¹⁰ using a 13 day exposure and the green line of mercury, obtained a Raman spectrum with liquid chlorine. This completes the data necessary to summarize the behavior of the halogen series in fluorescence. In iodine there is strong absorption, and a strong resonance spectrum is developed. In bromine the absorption is much weaker, and the resonance spectrum is accordingly very weak. In chlorine the absorption has become so weak that it is no longer possible to excite a resonance spectrum. Instead, with the use of the high concentration which the liquid state provides, a Raman spectrum is obtained.

The writer is deeply indebted to Professor R. S. Mulliken for his interest and valuable advice, and to Professor G. S. Monk for his helpful suggestions in points of experimental procedure. The work of Mr. Van Hesperen in constructing the mercury arcs, which were exceptionally efficient, is much appreciated by the author.

¹⁰ S. Bhagavantam, *Ind. J. Phys.* **5**, 37 (1930).

